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Direct and simultaneous determination of metal impurities in catalysts based on platinum group elements

Research Article

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Abstract: Production of new catalysts requires effective analytical quality control. The study of trace element composition of heterogeneous catalysts, based on C+PdO, using atomic emission spectrometry (AES) was carried out. A new method for the direct solid-state analysis by means of AES with direct current arc discharge was developed. On the basis of the qualitative analysis of elements, Al, Fe, Ni, Si and Ti have been identified, and for these elements, the quantitative method of determination has been developed. Optimization of excitation parameters and validation of the analytical method are presented. Calibration samples of the following composition were prepared: graphite powder (as a matrix), 3% of PdO and increasing contents of determined element oxides (spectrally pure). Calibrations were calculated by means of the least squares method. Working range for element impurities was from 1% to 0.0003%, and the limits of quantification – LOQ, (10-σ criterion) varied in the range from 0.002% (Ti) to 0.0038% (Si). For the control of active component, palladium was calibrated (working range – 0.01%-10.00%; LOQ -0.027%). The developed method can be used, also, for the elemental determinations of the other carbon based catalysts with the different active components (of platinum group elements).

Keywords: *Palladium catalysts • Trace element composition • Solid-state analysis • DC arc spectrometry*

1. Introduction

During the last century, the catalytic properties of platinum group elements (PGEs) have found widespread applications in the chemical industry. They have also been used to minimize the emission of pollutants from combustion engines during their operation.

Catalytic converters contain valuable materials. The active component of an automotive catalytic converter may be a small quantity of noble metal (Pd, Pt or Rh), and the trace elements of Ce, La, Fe, Ni, and Cu, which also have catalytic effects. Others metals also can be present: *e.g.* Pb, Mn, Zn, and they are contaminants which cause poisoning of the catalyst.

Most catalytic converters today consist of palladium or a combination of palladium and another noble metal (platinum, rhodium and the others). This composition gives a good compromise between cost and performance. Palladium is currently the cheapest of the three metals and has excellent activity for the oxidation of hydrocarbons as well as very good thermal durability. In addition, with a well-designed converter, palladium can also have a very good activity for the removal of nitrogen oxides. Drawbacks to palladium include its sensitivity to poisonous elements.

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Composition of catalysts, in particular, the content of trace elements and metallic impurities, significantly affect their properties. Then, development and production of the palladium heterogeneous catalysts are connected with requirements on the analysis of their major and minor element composition.

There are lot of methods in analytical chemistry which can be used for element determination of catalysts. Many of them involve wet chemistry; so these methods are destructive, require considerable time and labor and produce a hazardous waste. The methods of quantification used were mostly adapted from conventional spectroscopic procedures.

The published and routinely used methods include X-ray fluorescence spectrometry [1-5], and inductively coupled plasma atomic emission spectrometry [6,7] with mixed acid digestion (digestion usually uses a mixture of mineral acids). From the 1970's, the improved detection limits of graphite furnace atomic absorption spectrometry permitted element determination in these kinds of materials [8], and later, flame AAS determinations was also applied [9]. More recently, the flow injection on-line electrothermal atomic absorption spectrometry of rhodium determination was used [10]. However, the dissolution of these kind of materials is very difficult, and it produces possible sources of systematic errors. Instrumental neutron activation analysis provides the possibility of direct solid state analysis, but it is not routinely applied [11,12]. Glow discharge atomization in atomic absorption spectrometry also offers an alternative through direct atomization from the solid state [13]. The first application of inductively coupled plasma mass spectrometry to PGEs in catalysts occurred in the 1990's [14-17], and around the same time, the analysis using glow discharge mass spectrometry was published [18]. The ICP MS analysis applying internal standardization and isotopic dilution has been used in the past up to present times [14,19,20]. For the two-dimensional multi-elemental compositional mapping and in-depth analysis of the poisonous elements in catalysts, laser induced breakdown spectrometry was applied [21].

Direct current (DC) arc optical emission spectrometry has some key advantages over the above mentioned methods: First, it requires minimal sample preparation. Second, after optimization of the calibration process, the routine measurement takes approximately 1 minute per item and provides information about multi-elemental composition. Third, in comparison with other methods, it is very cheap. DC arc spectrometry provides element screening and allows comparison with other methods to validate the experimentally obtained results. Therefore, the development of a fast and cheap analytical method for the determination of trace element contents in the industrial and automotive catalysts is very important. Graphite arc emission spectroscopy is one of the appropriate methods for this purpose.

The majority of the available papers dealing with the determination of the major and minor element components of catalysts are very old [1,2,6-9, 11-18,21,22], and they are usually focused on more expensive analytical methods, *e.g.* ICP OES, and ICP MS [6,7,14-17,19,20,22,23].

There is also a lack of papers about DC arc spectrometric analysis of catalysts which is the reason for development of this method. Its validation can be justified as follows: it is cheap, environmentally acceptable, and it is required as a tool for quality control by catalyst producers. In accordance with the qualitative analysis of the studied carbon based catalysts, a method for the determination of aluminum, iron, nickel, silicon, and titanium has been developed which may be present in the catalyst products in trace amounts. The developed method can be used also for the elemental determinations in similar carbon based sample matrix.

2. Experimental procedure

2.1. Instrumentation

The novel types of DC arc spectrometers with Echelle-optics, semiconductor array detectors, and electronically controlled high current arc generators, have become possible as a tool for analysis of the insoluble solid state materials of different origins.

The optical spectrometer, model AtomComp 2000, produced by Thermo Scientific (Thermo Jarrell Ash Corporation, USA), was used, equipped with Echelle optics and CID (Charge Injection Device) solid state detector. Echelle optical system with 52.65 groove mm^{-1} of Echelle grating is combined with a cooled CID sensor composed of a 512×512 pixel array. The spectrometer provides coverage of the wavelength range from 175 to 800 nm. CID camera controller operates all spectrometer hardware functions and information is transmitted to a compatible computer. The readout system is capable of acquiring data from the entire photo active area simultaneously.

Operations are controlled by ThermoSpec software. Gross line intensities can be corrected for the corresponding backgrounds at selectable wavelengths, and the net line intensities are automatically calculated for preselected integration time for the purpose of analytical curves. The Echelle optics produce a two dimensional spectrum which is focused on a CID detector. This design allows the production of digital readout of the entire spectrum.

Table 1. Experimental conditions for the work with spectrometer Atomcomp 2000.

Spectral working range	175 – 800 nm
Kind of imaging (display)	direct with one lens
Excitation source	computationally-controlled integrated DC arc
Primary voltage	220V
Current intensity	6 - 18 A
Exposure time	6 + 19 + 40 s
Type of electrodes	sample electrode – type SE 232, (anode); counter electrode – the same material; producer: Elektrokarbon-Topoľčany (Slovakia)
Electrode distance	4.00 mm
Analytical signal	integrated intensity of the fixed-to-limits integration (optional pixels)
Evaluation of the signals	software ThermoSpec / CID detector

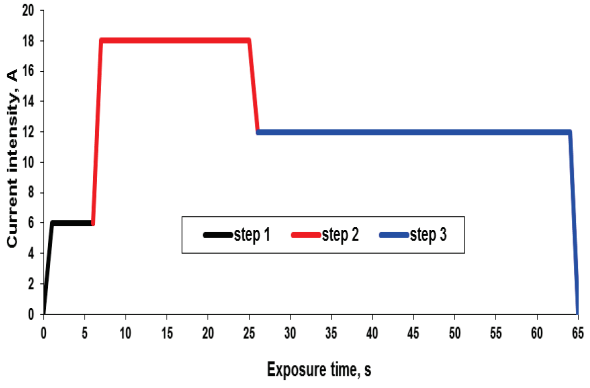

Figure 1. DC arc exposure program, optimized arcing conditions.

In a single reading, accurate simultaneous measurements may be made on both intense and faint spectral lines.

Double optics is used to decrease the negative effect of arc wandering on image stability. The applied spectrometer makes possible the time resolution of spectra, which can be made simultaneously (the "time-scans" mean – line intensity *versus* arcing time plots) [24].

The DC arc generator was applied providing the variable arc current up to max. 36 A. The electrode gap was set to 4 mm before starting the arc, and it was not readjusted during arcing. The selected currents were 6, 18 and 12 A (Fig. 1). The counter electrode was made of electro-carbon material (rod shape with rounded end; diameter - 6 mm) with the same thermal conductivity as the sample electrodes and with the highest spectral purity. Counter electrodes can be reused after cleaning by 10 s post-arcing. The sample electrodes have a cup shape cavity; the length of electrode is 38.1 mm, and the electrode form is characterized by cup sizes as follows (in mm): external diameter of the cup - 4.97; height (of the cup) – 4.00; wall thickness – 0.5; neck diameter of the cup (undercut) - 3.00; neck high of the cup (undercut) – 0.15. The arcing is continued until complete vaporization of the filled sample amount (15 mg of sample) with the simultaneous consumption of the electrode cavity and the cup wall.

2.2. Preparation of calibration standards and samples

For sample preparation, spectrally pure materials were used: graphite powder from Elektrokarbon-Topoľčany (Slovakia), type – SU 601, PdO from Merck (Germany) and the element oxides from Johnson-Matthey (United Kingdom).

Calibration standards were prepared with the model matrix corresponding to the real catalyst samples. Basic mixture, as the model matrix for calibration standards, contains graphite powder and 5% of PdO (50000 μg g^{-1} of PdO - throughout the article, the content is expressed in weight percent, from this point forward - %).

Micro-heterogeneity and sufficient weight of the samples (more than 10 mg) are needed for acceptable precision of the analyses [25]. The weighed amounts of the samples and standards were 15 mg; therefore, the basic condition for precision was fulfilled. The samples were also milled for 45 min to ensure more than 40% portion of the sample had a grain size below 20 μm [26].

With regard to the required working range of the method and the expected impurity content in the catalysts, the following element concentrations of the standards were selected. Calibration standards of all determined elements (Al, Fe, Ni, Si, Ti and Pd) were prepared as eight samples having increasing concentrations of the metals in the basic mixture: 0.0003% (3 μg g^{-1}), 0.001% (10 μg g^{-1}), 0.005% (50 μg g^{-1}), 0.01% (100 μg g^{-1}), 0.05% (500 μg g^{-1}), 0.1% (1000 μg g^{-1}), 0.5% (5000 μg g^{-1}), and 1% (10000 μg g^{-1}).

The special control standards for accuracy evaluation were also prepared: 1st graphite powder containing 0.5% PdO without the presence of elements; 2nd graphite powder containing 0.05% of all studied elements without the presence of PdO. These control standards were used as the intra-laboratory reference materials (LRM) for quality control of analysis (CRM of suitable composition is not commercially available).

The same control samples (as the blanks) were used for the LOD and LOQ evaluation:

For LOD (LOQ) of the studied elements, a control sample without studied elements was analyzed (containing only matrix and Pd); and for LOD (LOQ) of Pd using a sample without Pd was utilized (containing only matrix and analytes).

The real samples of catalysts (based on "C+PdO mixture") and the raw materials required for catalysts production (*e.g.* Norit) were also analyzed in this study. They were filled directly into electrodes without any other treatment.

From the above mentioned standards and real samples, 15 mg was placed in the electrode cavity and pressed with a well-fitting plastic rod. The precision in the weighing of standards and samples (5 replicates) has been expressed by relative standard deviation (RSD), and has not exceeded 5%.

2.3. Statistical analysis and validation parameters

The experimental data were processed using Microsoft Excel 2010. The calibration data were analyzed by linear and quadratic regressions to fit the following model:

Linear: $\sum I = Y = A + B \times c(Me)$

Quadratic: $\sum I = Y = A + B \times c(Me) + C \times c^2(Me)$

Where c - is concentration, $\sum I$ - is the average intensity. Y- represents the response function; A - is the intercept; B and C- are the linear and quadratic terms, respectively.

The relative standard deviation of the method (RSD_{met}), as the parameter of precision, was calculated according to the following equation [27]:

$$RSD_{met} = \frac{1}{B} \times \frac{s_{res}}{\bar{c}} \times 100/\%$$

Where s_{res} - is residual standard deviation, $\bar{c}$ - is the average concentration (in the middle of the working range).

RSD_{met} is also usable as criterion of the robustness of the method (stated on p. 164 of [27]).

Recovery, as the accuracy validation parameter, was calculated according to the following equation (mentioned on the p. 172 of [27]):

$$Rec = \frac{c_{exp}}{c_{teor}} \times 100/\%$$

Where *REC* – is Recovery in %, c_{exp} – is experimentally determined concentration, and c_{teor} – is concentration of the prepared standards (special control standards).

Limits of detection (LOD) and limit of quantifications (LOQ): For the calculation of LOD, 3σ criterion of the blank sample was used (and 10σ criterion for the calculation of LOQ). Sample blanks were prepared as mentioned in the subsection 2.2. LOD was calculated according to the following equation:

$$LOD = \bar{x}_0 + 3\sigma$$

Where *LOD* – is limits of detection, $\bar{x}_0$ – is the average of the analytical signal of the blank sample, σ – standard deviation of the blank signal.

3. Results and discussion

3.1. Optimization of excitation conditions

The DC arc generator used allows the variation of current intensity which determines the arcing temperature. Requirement for the choice of excitation parameters of the free burning arc was a complete vaporization of the loaded sample (together with the consumption of electrode cup wall) which had to be attained in 65 s of arcing time. The selected currents were 6, 18 and 12 A (see Fig. 1). The excitation of the calibration standards and samples was made under the conditions listed in the Table 1.

The total evaporation of analytes was additionally verified by the post-arcing of the exposed sample electrodes, where no intensity signals of studied elements have been registered [28]. Such verification of total vaporization is unique, and it has never been used and published in analytical practice.

3.2. Selection of spectral lines

The ThermoSpec program makes possible the visual inspection of the preselected spectral ranges (intensity versus wavelength scans) for the background values on either of side of the spectral lines to be corrected. Software also allows selection of the most appropriate lines on the basis of a greater number of validation criteria. The general practice with this instrumentation is the selection of 2 or 3 spectral lines of each element in a preliminary study of the calibration curves. With regard to the proportionally increasing intensities of the pure signals according to the concentrations of analytes, the most suitable spectral lines were selected for analytical calibrations of studied elements. The data of the spectral lines [29] chosen during the method optimization are listed in Table 2. The spectral lines used for final calibrations are listed in Table 3.

The method for the trace element determination was developed; and for that reason, the most intense spectral lines of each element were selected in the preliminary

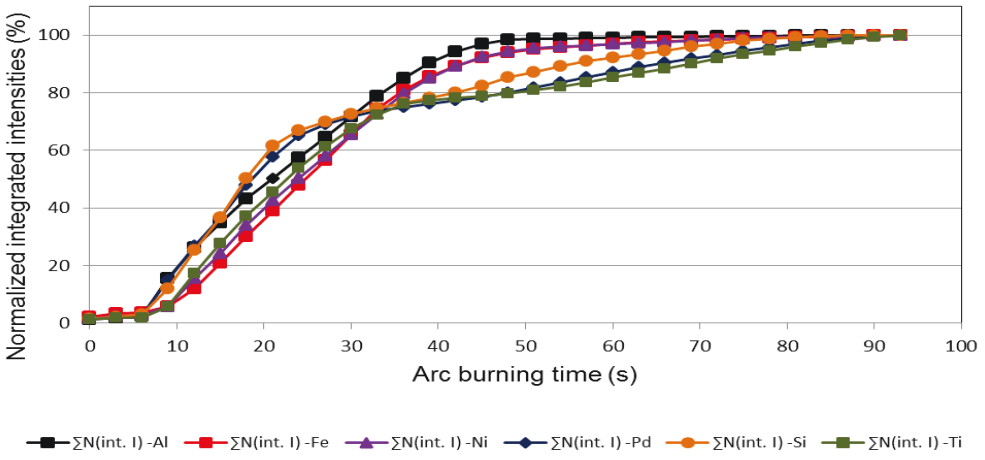

Figure 2. Time-scans of normalized integrated intensities in 90 s arcing time for the elements: Al (λ=308.2 nm), Fe (273. 9 nm), Ni (345.8 nm), Pd (340.4 nm), Si (288.1 nm), Ti (336.1 nm).

Table 2. The data of the spectral lines (Al, Fe, Ni, Si, Ti, Pd) chosen during the method.

Element/ionization state/wavelength (nm)	$E_{excitation}$ (eV)	Intensity (Meggers) [29]
Al I 237.312(109)	5.22	36
Al I 257.510(101)	4.81	48
Al I 308.215 (84)	4.02	320
Al I 309.271(84)	**4.02**	**650**
Al I 394.401(66)	**3.14**	**450**
Al I 396.152(66)	**3.14**	**900**
Fe II 259.940(100)	**4.77**	**200**
Fe I 261.187 (99)	4.79	80
Fe II 273.955 (95)	5.51	75
Fe I 371.994 (70)	**3.32**	**600**
Ni I 345.847 (75)	3.80	460
Ni I 349.296 (74)	**3.65**	**500**
Ni I 341.476 (67)	**3.65**	**750**
Si I 288.158 (90)	**5.08**	**260**
Si I 252.851 (103)	4.93	200
Si I 251.612	**4.95**	**360**
Ti I 307.297 (84)	4.04	95
Ti 307.864 (84)	**4.06**	**190**
Ti II 336.121 (77)	**3.71**	**600**
Pd I 340.458	**4.46**	**2600**
Pd I 342.124	4.58	1400
Pd I 363.470	4.23	2200

study (see Table 2, intensities in bold). The resonance spectral line could not be applied due to Pd being in the higher concentrations. However, the preliminary calibrations showed that the use of the most intensive lines did not result in precise measurements (RSD_{met}), and appropriate accuracy of the method (recoveries of the used LRM). For this reason, some of the spectral lines were omitted from further study (see Table 3).

3.3.Time-scans of spectra

The time-scans of spectra provide basic information on the selection of optimum analytical conditions and in understanding of the main features of the vaporization process. The standard of 0.1% concentration was used for these studies and contained all studied element impurities and Pd. The optimized arcing conditions (Table 1, Fig. 1) were estimated primarily on the basis of time-scans of spectra, and secondly, by the evaluation of the recoveries of the laboratory prepared control standards.

The presented time-scans are averages of the five replicates of each measured sample (standard with concentration 0.1%). The curves in Fig. 2 show the increase of normalized integrated line intensities with the arcing time (each line normalized separately), and the time-scans of spectra were the basic information required for the specification of the sparking-time duration. For the sake of brevity, the time-scans of the spectra for all studied elements are shown in one diagram, see Fig. 2 (100% means the complete evaporation of element).

The shape of time-scans of spectra are typical for arcing in the graphite electrodes, and the differences of values of normalized integrated intensities at the end of burning are caused by differences in volatility of studied

Table 3. The basic metrological and validation characteristics of the developed method; LOD, LOQ - expressed in weight percent (%).

Element line λ(nm)	R^2	RSD_{met}(%)	LOD (%)	LOQ (%)	Recovery (%)
Al 237.312(109)	**0.9914**	**7.0**	**0.0230**	**0.0340**	**112**
Al 308.215 (84)	**0.9981**	**3.3**	**0.0099**	**0.0167**	**122**
Al 309.271(84)	0.9993	2.8	0.0060	0.0101	131
Fe 273.955 (95)	**0.996**	**4.8**	**0.014**	**0.023**	**126**
Fe 259.940 (100)	0.9855	9.1	0.016	0.052	159
Ni 345.847 (75)	**0.9988**	**0.16**	**0.019**	**0.053**	**108**
Ni 349.296 (74)	0.9991	2.27	0.039	0.097	135
Si 288.158 (90)	**0.993**	**6.2**	**0.006**	**0.0185**	**88**
Si 252.851 (103)	0.9926	6.3	0.008	0.027	74
Ti 307.297 (84)	0.9984	3.0	0.139	0.218	75
Ti 336.121 (77)	**0.9945**	**5.6**	**-**	**0.0024**	**102**

elements [30]. For refractory impurities, reproducibility is typical worse in the intensity measurements and is related to their vaporization losses (see evaporation characteristic of Ti, in Fig. 2)

The finally chosen time of arcing corresponds

- to the evaporation characteristics of the elements,
- to burning time (consumption) of the electrode body,
- and to the acceptable validation data of the developed method.

3.4. Analytical calibration, performance of the data

Calibration and determination of real samples was performed on the spectral lines, which are marked in bold, see Table 2.

The analytical curves (net integrated line intensities versus analyte concentrations) were determined through linear and quadratic regression calculations and are demonstrated for Al, Fe, Ni, Si, Ti and Pd in Fig. 3. Five replicates of the arcing, for all standards and samples were performed, and correlations of the linear fits of all data points are characterized with an average coefficient of R^2=0.9947. The crossing points of the ordinates and corresponding equations (Fig. 3) suggest acceptable background correction and accuracy of the concentration values of laboratory standards [31]. The correlation coefficients and the basic validation characteristics are listed in the Table 3.

Preliminary measurements and the first calibrations showed that the use of the most intensive lines did not always yield the best analytical results [31]. Therefore, for the next calibrations, some spectral lines were omitted (see Table 2 and Table 3). Then, calibrations were realized on the spectral lines that show the best validation parameters in all three calibration ranges: 1st - c_{max}-c_{min}: 1.0-0.01%; 2nd - c_{max}-c_{min}: 0,1-0.001%; 3rd - c_{max}-c_{min}: 1.0-0.0003%. For clarity, the calibrations (Fig. 3) and validation parameters (Table 3) are presented only for final (total) - 3rd calibration range:

-All studied trace elements were calibrated in concentration region 1.0-0.0003%.

-The presented working range of Pd is 10.00-0.01%; and limit of quantification (LOQ) was -0.027%.

For the next routine analyses the calibration on the following spectral lines will be recommended: Al 237.312 (109); Al 308.215 (84); Fe 273.955 (95); Ni 345.847 (75); Si 288.158 (90); Ti 336.121 (77).

Precision parameters expressed as the relative standard deviations of the method (RSD_{met}) were from 0.16 to 7.0% (on the selected lines, marked in bold - see Table 3) which is a very good result in the area of the solid-state analysis. The precision parameters on the other spectral lines do not overlap, 9.1% (RSD_{met}), and can be evaluated as a good to excellent result.

Precision was also controlled by the repeated measurements of the real catalyst samples (5 replicates). The relative standard deviations of normalized integrated line intensities were in the interval of 0.7-15%, which is an acceptable result for solid state analysis. RSDs could be influenced by the quality of raw material (e.g. Norit), which was used for the manufacture of catalysts (compare Cat1, Cat2 with Cat3, Cat4, and Cat5). The results of the real samples analyses are presented in the Table 4. The intensity values are presented (Table 4), and the corresponding elemental contents of real catalyst samples, expressed in weight percent (%), are as follows: between 0.12 and 0.20% for Al, 0.05-0.20% for Fe, 0.013-0.018% for Ni, 0.48-0.75% for Si, and 0.008-0.023% for Ti (see intensity values of Cat1, Cat2, Cat3, Cat4, and Cat5, in Table 4). On the basis

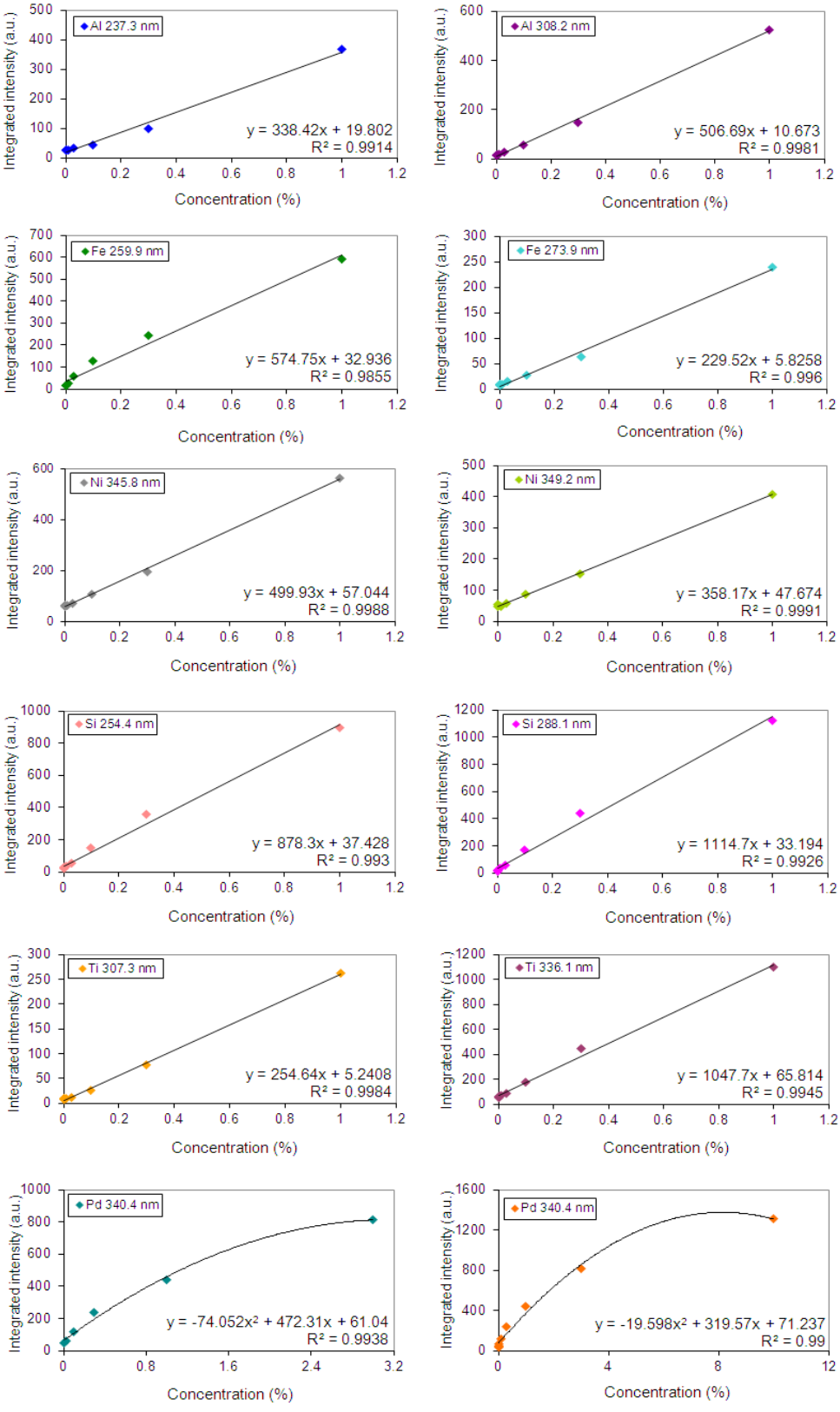

Figure 3. Analytical calibrations for trace elements (Al, Fe, Ni, Si, Ti); and active part of catalysts (Pd).

Table 4. Results of the real catalysts samples Cat1 – Cat5, and precision control expressed as RSD (%) of the repeated measurements (presented the intensity values ± standard deviation of the measurements of real catalysts samples Cat1 – Cat5).

Element line λ(nm)	Cat1 ± SD	RSD (%)	Cat2 ±SD	RSD (%)	Cat3 ±SD	RSD (%)	Cat4 ±SD	RSD (%)	Cat5 ±SD	RSD (%)
Al 237.3	95.4±8.8	9.3	111.5±11.3	10.2	71.7±2.3	3.2	75.2±2.7	3.5	91.0±2.8	3.1
Fe 273.9	19.2 ±1.7	8.6	52.0±7.8	15.0	18.2±0.9	5.4	20.0±0.4	2.2	21.6±1.1	4.9
Ni 345.8	65.8±1.6	2.5	63.5±0.7	1.1	65.3±0.4	0.6	65.7±0.6	0.8	65.1±1.3	2.0
Si 288.1	634±57	9.0	873±64	7.3	570±39	6.9	606±38	6.3	749±45	6.0
Ti 336.1	74.0±1.8	2.4	89.9±0.6	0.7	81.6±3.1	3.8	74.3±1.6	2.1	80.9±2.3	2.9

of the intensity values, the element contents can be calculated according to the equations shown in Fig. 3.

As accuracy parameters, recoveries of the used LRM on the chosen lines, were estimated (Table 3). The special control standards as the laboratory reference material were prepared for this purpose.

Acceptable recoveries are dependent on the element content. Recovery values of elemental contents, less than 1%, should range from 95 to 105% [27]. The method was validated for the direct solid state element determinations on the significantly lower levels than 1%, so there are observed the values outside the recommended interval (Table 3).

It should be noted that in the case of Pd (calibrated in the range 0.01-10.00%; LOQ- 0.027%), the calibration line is curved at higher concentrations. This is probably due to self-absorption and "saturation" of the detector by high intensities of radiation. The use of the weak spectral lines of palladium is complicated by coincidence with other elements.

However, atomic spectroscopy is not suitable for the determination of the concentrations greater than 1%. In the concentration range below 1%, suitable (linear) calibration lines can be obtained. In this case, Pd was calibrated only for informative control of Pd content in various hydrogenation catalysts.

4. Conclusions

The new analytical method by means of optical emission spectrometry with direct current arc discharge for determination of trace element contents in catalysts was developed and validated. The presented study has produced the analytical optimization, calibration data, and assessment of the quality control. The precision of the method has brought good to excellent results. Accuracy parameters yield to acceptable agreement with reference values of the control standards.

Calculated limits of detection and quantification also correspond to the requirements for the routine analyses and quality control of the catalysts' production. The presented information could be applicable to the appropriate field of analytical praxis. Published analytical methodology satisfies the demands of a fast and cheap routine analysis of industrial and automotive catalysts in following aspects:

First, it is practically a non-invasive method. Second, it provides a method for direct analysis of solid state materials, and third, it fulfills basic criteria of sustainable chemistry.

It is therefore most appropriate for the purposes of routine measurements in the area of catalyst research and production.

The presented work also challenges the development of appropriate reference materials. Despite the demand from the area of the catalyst production, there is a lack of reference catalyst matrixes with the certified composition of trace elements. There are required analyses of many more real samples of varied composition, evaluation of robustness, repeatability, reproducibility, and joining of the individual economic possibilities of academic and applied research.

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